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(54) Title of the Invention : Packing for Purification Equipment of Automotive Exhaust Gas

(21) Application Number : J.P. Sho. 56 - 112413

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(65) Kokai (Laid Open) Number : J.P. Sho. 58 - 13683

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(57) Claim

1. In the packing for the purifying device of automotive exhaust gas comprising of a vermiculite sheet and a ceramic fiber sheet by lamination, a packing for the purifying device of automotive exhaust gas which is characterized by aforesaid vermiculite sheet comprising a mixture of expanded vermiculite particles, unexpanded vermiculite particles having a particle diameter of more than 35 mesh and organic elastic binder having a weight ratio of 1:2 to 1:5 being mixed and formed into a sheet under pressure with the required surface density, and aforesaid ceramic fiber sheet where ceramic fiber comprising a composition of alumina and silica having an average fiber length of more than 50 mm and an average fiber diameter of 2 to 4 μ m being formed into a sheet with binder which is combined with natural rubber and polybutene (phonetic: Translator's Note : this should be polybutene).

Detailed Explanation of the Invention

This invention relates to the packing for the purifying device of automotive exhaust gas, and this invention especially relates to the improvement of packing which is structured with expandable sheet material comprising vermiculite as the raw material.

Expandable sheet material comprising vermiculite as the main material (or packing punched and cut processed) has excellent heat resistance to high temperature, and it also has a property by which it expands with heat (called volume expansion), therefore it is marked as the packing material for filling machines which handle high temperature, and its usages and development have been done.

For instance, in the purifying device for automotive exhaust gas structured by accommodating a ceramic made monolith type catalyst where a noble catalyst is carried in a metal cylindrical container, aforesaid expandable sheet is used for the filling between the monolith type catalyst (hereinafter it is abbreviated as monolith) and the cylindrical container (hereinafter it is abbreviated as external cylinder), or it is used as the retaining material which supports the monolith.

As aforesaid monolith used for aforesaid purifying device for automotive exhaust gas, it comprises of a ceramic base material having a low thermal expansion coefficient to the extent of $1.2 \times 10^{-6}/^{\circ}\text{C}$, and an extrusion molded product having a honeycomb wall to the extent of 0.15 mm to 0.3 mm is most suitable to respectively satisfy the three requirements of heat resistance, resistance to shock and multi-contact surface area, but there is technical difficulty with this whole purifying device because there is a large gap between the thermal expansion coefficient and the degree of shrinkage of the monolith and the external cylinder, therefore a special device to retain the monolith in the external cylinder is necessary.

Especially, recently there has been a tendency to increase the instance of using an exhaust gas purifying device in the neighborhood of the engine exhaust manifold part which has a higher temperature, and in this case heat resistance steel having a thermal expansion coefficient 1.5 times that of cast steel is adopted to aforesaid external cylinder material, and also to seek an improvement in the capabilities of aforesaid three requirements; in the case of considering the adoption of a monolith where its honeycomb wall is thin and strength is weak, packing which has an abundance of cushioning and is softer than conventional is required; furthermore, for the reason of improving the capabilities of the monolith, the sealing properties of gas to avoid the bypass of unpurified exhaust gas between the monolith and the external cylinder has been strictly required.

As the retaining material of the packing for a monolith which can partly or completely satisfy aforesaid requirement, various materials and structures have been proposed; in one of these, elastically retaining it with a spring and a bellows made of heat resistant steel, or where the fine metal of the same material is knitted and compression molded are partly utilized as the retaining material having elasticity, but there is a disadvantage where the temperature of the carrier often overheats by abnormal exhaust gas, and when this high temperature becomes more than 600°C, the metal of the bellows molded spring loses the elasticity, the role of the retaining material cannot be done, furthermore, the monolith becomes unstable by the pressure of the exhaust gas and the vibration of the engine, etc., and it will finally break. Also, aforesaid fine metal molded has a disadvantage because it is too rough to seal exhaust gas, and therefore complete purification cannot be expected.

Also, as means which do not use metal materials, a means where inorganic fiber material is packed between the monolith and the external cylinder has been proposed, and it has the advantages of having high heat resistance temperature, and it is also able to completely seal the space between the monolith and the external cylinder, therefore untreated exhaust gas does not leak, etc., but for the monolith to effectively be retained for a long period under the vibration of the engine and at the time of driving and also for the heating and cooling cycle, it is necessary for the packing density of the packing to be sufficiently high, also a special external cylinder, for instance, a multi-divided type metal cylindrical container is used for the packing, the thick mat state fiber material wrapping the interior of the monolith is strongly compressed, and it is fixed with a screw or a band, etc.; this purifying device becomes complex, and therefore this means also has disadvantages.

In consideration of improving aforesaid means, there is a means which uses packing in which vermiculite particle is mixed in inorganic fiber material, this is packed between the monolith and the container, the vermiculite is then expanded by the exhaust heat of the

engine and the inorganic fiber material is strongly compressed, and the monolith is retained by this which has been proposed, and it is partly utilized.

But even in the case of using this packing mixed with vermiculite, when the monolith is securely retained under severe actual driving conditions, it must be packed by strong compression to the extent of 50 to 60% of the packing thickness, its strong compression action breaks the side wall of the monolith, and accidents occur often.

Also, by usage of the property of the thermal expansion of the vermiculite particles, the vermiculite particles are made into a sheet, and a sheet laminated with this and ceramic paper has been proposed in this invention, and this packing shows excellent durability of its retaining strength, but this material is stiff, and the packing amount is determined by measuring the dimensions of the external diameter of a monolith having large dimensional tolerance, and it is rolled and inserted; however there are complicated processes.

The present inventors have examined the advantages and disadvantages of aforesaid various packing, and this invention was presented for the purpose of developing packing which possesses softness by utilizing the characteristics of vermiculite sheet which manifests large durability of its retaining strength proposed by the present invention and can be easily inserted into the narrow space between aforesaid monolith having large dimensional tolerance, and the external cylinder retains the monolith, and it maintains its retaining strength for a long period under repeated variations in space dimension with thermal expansion by high temperature at the time of exhaust gas purification and cooling cycle at the time of a stopped engine.

Furthermore, this invention was accomplished by the attention given to the vermiculite particle sheet presented by the present inventors and sheets such as fiber sheet, etc., being able to be separately prepared, and in the preparation of the vermiculite sheet, with regard to granules which are technically impossible to mix has also been examined, also with regard to various ceramic fibers, durability tests under circumstances which are close to actual utilization have repeatedly been done, and the result is that variation in retaining strength tested after a long period has been recognized even in those having unidentical initial retaining strengths, it has been recognized that only ceramic fibers in a certain range show excellent capability, also by the combination of natural rubber and polybutene as the elastic binding material of the ceramic fiber layer, it has been found that it can be endowed with flexibility and flexing resistance which have suitable fitness in the actual insertion device, and this invention was accomplished on the basis of this knowledge.

The vermiculite used in this invention is one kind of mica mineral; when it is heated, it expands to more than a few hundred times and it becomes a book state or accordion state, and granule state vermiculite having excellent noise absorption and thermal insulation properties has been known, and various organic or inorganic binding materials mixed with this is used in large quantities to building materials, fire resistant materials, etc.

Also, plate state vermiculite which is packed in the space of the iron plate, etc., and is thermal expanded has excellent cushioning, and its usage as the retainer of the monolith for the purifying device of automotive exhaust gas has been proposed before by the present inventors.

These vermiculites are now available as a product of the Parabola in South Africa and as a product of Montana in North America are used. The properties of these vermiculites are shown in Table 1.

Table 1

In South Africa	Product of Parabola	Product of Montana	
Size 4	3~7 mesh	#1	3~10 mesh
Size 3	5~12 mesh	#2	8~14 mesh
Size 2	9~24 mesh	#3	10~35 mesh
Size 1	16~42 mesh	#4	28~65 mesh

Also, the ceramic fiber used in this invention is alumina and silica having a weight ratio of approximately 1 melted in an electric oven, and it is made into fine fiber by the usage of high speed air flow or high speed rotating disc.

According to the objective heat resistance temperature, the compounding ratio of Al_2O_3 • SiO_2 is changed, and according to the temperature of the solution and the fibering method, these ceramic fibers are produced as an aggregate bark having a fiber length of 25 to 250 mm and a fiber diameter of 1.5 to 6 μ , and it is used as high temperature thermal insulation material at a glass softening temperature of approximately 850°C and a usage temperature of 1100 to 1500°C in the form of a paper blanket, textile product, etc.

The packing to retain the monolith type catalyst which is fundamentally the vermiculite sheet has been proposed before by the present inventors, that is to say, a mixture comprising of unexpanded vermiculite granule, forming the expanded vermiculite granule and organic elastic binding material into a sheet under pressure having a thickness to the extent of 0.5 to 1.5 mm, especially selecting vermiculite having prescribed diameter, and laminating a sheet comprising of ceramic fiber and special binding material onto one

side surface or both surfaces of the sheet having flexibility are the characteristics of this structure, and the retaining strength can be maintained by this structure under severe usage conditions.

In the packing for the purifying device of automotive exhaust gas comprises a vermiculite sheet and ceramic fiber sheet by lamination, the essential of this invention is packing for the purifying device of an automotive exhaust gas where aforesaid vermiculite sheet comprises a mixture of expanded vermiculite granules, unexpanded vermiculite granules having a granule diameter of more than 35 mesh and organic elastic binder having a weight ratio is 1:2 to 1:5 are mixed and formed into a sheet under pressure with the required surface density, and aforesaid ceramic fiber sheet where ceramic fiber comprises of a composition of alumina and silica having an average fiber length of more than 50 mm and an average fiber diameter of 2 to 4 μ is formed into a sheet with binder combined with natural rubber and polybutene (Translator's Note : the Japanese original here says polybudene).

Next, the details of the content of this invention will be explained on the basis of actual testing.

As a typical example of the usage condition of the purification device of automotive exhaust gas where the packing by this invention was installed, the external diameter of the monolith was 94.5 ± 1.5 mm, the maximum temperature of the side wall of the monolith was 600 to 850°C, the inner diameter of the metal external cylinder was 100 mm, the maximum temperature was 300 to 350°C and an acceleration to the extent of 5G was received by the vibration of the engine.

The packing amount which packed the space (2.0 to 3.5 mm) between the monolith and the external cylinder was, the amount of bearing strength became more than the pressure resistance strength of the side wall of the monolith when the packing was compressed into a minimum space dimension of 2.0 mm, there was the fear that the monolith would break, and when the amount was less than that, the retaining strength of the monolith was lowered, therefore the thickness (surface density) of the packing determined when the bearing strength of the packing compressed into the minimum space dimension became the pressure resistance strength of the side wall of the monolith was the allowable amount of maximum packing.

To satisfy the aforesaid condition, the testing device and the testing material were examined, and packing (25 mm width) for the monolith was rolled onto the outer periphery of a silica glass cylinder having an outer diameter of 93 mm, the monolith rolled with the packing was inserted into a heat resistant steel cylinder having an inner diameter of 100 mm and a thickness of 6 mm through a jig and this was the testing device; a cover was put

onto this testing device, the shearing stress corresponding to the force (0.7 kg) that the monolith was pushed out by exhaust gas and the force (4.2 kg) which was estimated to be received when the monolith was vibrated with 10G was allowed to be applied, weight was loaded onto the heat resistant steel cylinder, heat application and cooling were done by adjusting the amount of power supply to raise the temperature of the external cylinder to 350°C taking 30 minutes than the inner part of the silica glass, and the amount of compressed air blowing from the inner part of the silica glass cylinder was adjusted to lower the temperature to 50°C for following 30 minutes, the procedure of this heat application and cooling process was one cycle and these procedures were done repeatedly, by 4.9 kg loading, a limit switch was operated when 2 mm shear occurred between the silica glass cylinder and the heat resistant steel external cylinder, and the number of heating and cooling cycles which were withstood was recorded, and the samples which withstood the heating and cooling cycle 50 times passed.

However, the thermal expansion coefficient of the silica glass cylinder was $0.5 \times 10^{-6}/^{\circ}\text{C}$, which was smaller than the monolith's $1.0 \times 10^{-6}/^{\circ}\text{C}$, and also its loading was large. These conditions are more severe than the conditions of an actual car.

The pressure resistance strength of the monolith was set to 25 kg/cm², and to determine the acceptable maximum packing amount and also to match the retaining strength of the monolith to the required test condition, the combination of the minimum amount of vermiculite and the maximum amount of ceramic fiber having cushioning properties were determined, ceramic fiber sheets and vermiculite sheets having the mixing amount shown in Table 2 stated below were prepared, compression tests were done on them, and the combination where the bearing strength was in the vicinity of 25 kg/cm² at a thickness of 2.0 mm which was the minimum dimension of the space of the external cylinder was selected.

Table 2

Samples	Surface Density of Ceramic Fiber Sheet	Surface Density of Vermiculite Sheet	Compression Stress of 2.0 mm Space
(A)	1.75 kg/m ²	1.0 kg/m ²	20.3 kg/cm ²
(B)	1.35	1.35	24.2
(C)	0.95	1.80	41.0

(the combination of ceramic fiber sheet and vermiculite sheet refers to the Practical Examples stated below)

According to the table shown above, when the surface density of the packing for monolith was 2.7 kg/m^2 , the combination in (B) was appropriate; in the case of (A), the amount of vermiculite sheet was small and the durability of the retaining strength of the monolith was insufficient, in the case of (C), the monolith side wall was broken when the monolith was inserted into an external cylinder more than the pressure resistance strength, therefore hereinafter samples having the surface density in (B) were used.

Next, the durability test of the vermiculite granules and the ceramic fiber which are the main structural materials of the packing in this invention was done.

For the vermiculite sheet, the brands shown in Table 1 were used, and for the ceramic fiber sheet, fibers having different average fiber length and average fiber diameter were used. The surface density of the ceramic fiber sheet and the vermiculite sheet were as stated above.

The results of the durability test by repetition of the heating and cooling procedure as described above are shown in Table 3.

Table 3

Fiber Length	Fiber Diameter	South Africa Product of Parabola		Product of Montana in North America			Comparative Example #4 28~65 mesh
		Size 3 5~12 mesh	Size 1 16~42 mesh	#2 8~14 mesh	#3 10~35 mesh	#4 28~65 mesh	
50 mm	6 μ	x (14)		\oplus	x (39)		
	2.2 μ	\oplus	x (9)	\oplus	\oplus	x (8)	x (32)

Fiber Length	Fiber Diameter	South Africa Product of Parabola		Product of Montana in North America			Comparative Example #4 28~65 mesh
		Size 3 5~12 mesh	Size 1 16~42 mesh	#2 8~14 mesh	#3 10~35 mesh	#4 28~65 mesh	
32 mm	1.5 μ	x (27)		x (45)	x (12)		
	6 m	x (4)		x (15)			
	2.2 μ	x (8)		\oplus			
	1.5 m	x (3)		x (9)			

- surface density of the vermiculite sheet 1.35 kg/m^2
- surface density of the ceramic fiber 1.35 kg/m^2
- the number in the parenthesis is the number of heating and cooling cycles
- X mark means 2 mm shear occurred between the silica glass cylinder and the external cylinder
- \oplus mark means shear did not occur in 50 times of the heating and cooling cycles

Generally large diameter vermiculite granule is effective, also it was confirmed that the long fiber length of the ceramic fiber and a fiber diameter in the vicinity of 2.2μ is excellent.

Also, in the case of mixing the vermiculite fine granules into the ceramic fiber (equality of combination and surface density of the sheet) which is a conventional technique compared with the examples of this invention, the durability of the retaining strength was insufficient, and it was confirmed that the packing for monolith could not be used under severe condition as shown by the comparative example in Table 3.

The packing by this invention comprises a vermiculite layer and a ceramic fiber layer as described above, and it is expected that the unexpanded vermiculite is expanded and becomes an expandable vermiculite sheet having elasticity and a thickness a few times that before expansion, therefore there is the expectation that the durability of the retaining strength is different when it is installed by contacting with the monolith side wall which is the high heat surface, and when the vermiculite layer is installed in the middle of the monolith side wall and the inner wall of the external cylinder, the laminated packing [ceramic fiber sheet $X \text{ kg/m}^2$ + vermiculite sheet $Y \text{ kg/cm}^2$ + ceramic fiber sheet $Z \text{ kg/m}^2$] laminated from the monolith side wall which has both density is prepared as shown in Table 4, and durability tests were done, and the result is it was confirmed that there was durability of the retaining strength only when (A) and (B) in the table were combined, that is to say, only when the vermiculite layer is close to the monolith side.

Table 4

	<div style="display: flex; justify-content: space-between;"> <div style="text-align: center;"> Monolith Slide External Cylinder Side </div> <div style="text-align: center;"> Fiber length Fiber diameter Vermiculite granule </div> </div>			50 mm 2.2 μ Product of Montana in North America	50 mm 2.2 μ Product of Montana in North America
	X	Y	Z		
A	0	1.35 kg/m ²	1.575 kg/m ²	⊕	⊕
B	0.20 kg/m ²	1.35 kg/m ²	1.35 kg/m ²	⊕	⊕
C	0.45 kg/m ²	1.35 kg/m ²	1.13 kg/m ² c	x (8)	x (19)
D	0.68 kg/m ²	1.35 kg/m ²	0.90 kg/m ² c	x (27)	x (21)

- the numbers in the parenthesis is the number of heating and cooling cycles
- X mark means 2 mm shear occurred between the silica glass cylinder and the external cylinder
- ⊕ means shear did not occur in the 50 times of the heating and cooling cycles

Next, the binder of the ceramic fiber is described.

In the packing in this invention, vermiculite having a surface density to the extent of 1.35 kg/m² in a sheet is necessary as described above, and with regard to a ceramic sheet laminated with this, the bulk specific gravity of a usual ceramic fiber blanket is 0.13 g/cm², its thickness is to the extent of 10 mm and it has weak strength, therefore it cannot be handled as the packing for monolith.

Also, while the bulk specific gravity of the ceramic fiber paper is 0.3 g/cm², it has a thickness of 4.5 mm and it has strength, but when it is laminated with aforesaid vermiculite sheet, its total thickness becomes to the extent of 6 mm, and when it is wound onto the periphery of the monolith, a stretching force is applied to the outer layer of the ceramic fiber paper, the binding on the vermiculite layer is peeled off, or wrinkle occurs on the vermiculite layer.

To solve these difficulties, various binders, for instance, rubber adhesive such as NBR, SBR, NR, etc., have been examined, and finally aforesaid difficulty does not occur when only NR and polybutene (PB) are combined.

That is to say, with regard to the binders combined with NR and PB as shown in Table 5 below are, even in ceramic fiber sheets having the same surface density, the thickness of the sheet can be thin, adherence with the vermiculite sheet is perfect even in the condition of

flexing to a 93 mm diameter of the monolith, it easily stretches as a sheet, and also cracking does not occur.

Especially, in the binder where the amount of NR and PB is increased to double shown by example g in Table 5, its layer is thin and its surface density is high, it has sufficient strength and sheet flexibility, and it shows a stretchable property, and a conventional ceramic fiber sheet like this does not exist.

Table 5

	binder				Thickness	Observation Flex to Monolith Periphery Diameter
	NBR	SBR	NR	PB		
a	7.5%				5.3 mm	occurrence of crack
b		7.5%			6.9 "	"
c			7.5%		4.5"	separation between the vermiculite layer and the ceramic fiber layer
d			5	2.5	4.3 "	"
e			2.5	5	4.0 "	Excellent
f				7.5	12.0 "	No overall capability
g			5	10	3.5 "	Excellent

The summarized results on the basis of the practical test data above is shown as the practical example described below.

Practical Example

0.6 kg bulk state ceramic fiber having an average fiber length of 50 mm and an average fiber diameter of 2.2μ was placed in a 100 l testing beater, it was heated for 5 minutes without loading the beater edge, and the shot precipitated bottom of the beater was removed, 0.45 kg ceramic fiber pulp was obtained, 45 g polybutene (HV-300, 100° less 32000 kinetic viscosity) manufactured by Nihon Sekiyu (KK) and 22.5 g natural rubber (LCS Lever Techs) manufactured by Lever Techs (phonetic) (both emulsion) were placed in this, it was allowed to set by adding a small amount of alumina sol • sulfate bond, this ceramic fiber pulp was made into a sheet by a 1 m x 0.33 m handmade paper machine, it was dried by compressing with a bearing strength of 10 kf/cm², and semi-wet powder which was mixed on this ceramic fiber sheet with:

size 3 expanded vermiculite granule (Product No. T/#5888 manufactured by Nichiasu

----- 0.1 kg

vermiculite granule #2 product of Montana in North America ----- 0.35 kg

NR (LCS Lever Techs 60% solid content) ----- 0.012 kg

water ----- 0.070 l

was uniformly spread at a thickness of approximately 5 mm with a roller, and both surfaces of the sheet were laminated thin sheet having a surface density of 0.2 kg/m^2 and it had the same combination as aforesaid ceramic fiber sheet on it held with a wire net, pressure was applied to it at a bearing strength of 15 kg/cm^2 , between the sheets was sealed with rubber latex oozing out from the vermiculite semi-wet powder layer, and this laminated sheet was dried, it was cut into tape having a width of 25 mm, and it was the packing for monolith.

Aforesaid packing was wound onto the outer periphery of a silica glass cylinder having an outer diameter of 93 mm which was supposed to the monolith, the monolith wound with the packing inserted into a heat resistant steel cylinder having an inner diameter of 100 mm and a thickness of 6 mm through an insertion jig was the sample, a cover was placed on this specimen, and a shearing stress corresponding to the 0.7 kg force that the monolith was pushed out by the exhaust gas and the force (4.2 kg) which it was estimated to receive when the monolith was vibrated by 10G was allowed to be applied, a weight of 4.9 kg was loaded onto the heat resistant steel cylinder, heat application and cooling were done by adjusting the amount of power supply to raise the temperature of the external cylinder to 350°C taking 30 minutes than the inner part of the silica glass, the amount of compressed air blown from the inner part of the silica glass cylinder was adjusted to lower the temperature to 50°C in the following 30 minutes, the procedure of this heat application and cooling process was one cycle and this procedure was done repeatedly 50 times, and even after that no shear occurred between the silica glass cylinder and the external cylinder, and it passed.

Also, the purifying device where aforesaid packing was packed to monolith with tape was integrated into a car engine, test of full engine revolution was done for 200 hours, and the result was that damage of the monolith was not recognized. Also, shear of the monolith was also not recognized.

As stated above, according to this invention, in the packing for the purifying device of automotive exhaust gas comprising a vermiculite sheet and a ceramic fiber sheet by lamination, aforesaid vermiculite sheet comprises a mixture of expanded vermiculite granules, unexpanded vermiculite granules having a granule diameter of more than 35 mesh and organic elastic binder having a weight ratio of 1:2 to 1:5 were mixed and formed into a sheet under pressure with the required surface density, and aforesaid ceramic fiber sheet where ceramic fiber comprises a composition of alumina and silica having an average

fiber length of more than 50 mm and an average fiber diameter of 2 to 4 μ was made into sheet with binder which was combined with natural rubber and polybutene (Translator's Note : the Japanese original says polybudene), therefore as the packing which is inserted and configurated into the space between the monolith and the cylinder of the purifying device for automotive exhaust gas, and packing which maintains a suitable retaining strength of the monolith for a long period in the case of repetitious variation of the space dimension thermal expansion by the heating and cooling cycle between the time of purifying the exhaust gas at high temperature and stopping the engine at ordinary temperature, by this, it can greatly contribute to improving the durability of the purifying device of automobile exhaust gas.

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1

2

⑳特許請求の範囲

1 パーミキュライトシートとセラミックファイバーシートとを張り合わせて成る自動車排気ガス浄化器用パツキンにおいて、前記パーミキュライトシートは、重量比で1:2~1:5に混合される膨張されたパーミキュライト粒と粒径35メツシユ以上の未膨張パーミキュライト粒及び有機弾性結合剤とからなる混合物が所要の面密度をもつてシート状に加圧成形されたものであり、前記セラミックファイバーシートは、アルミナとシリカとからなる組成で平均繊維長50mm以上、平均繊維径2~4μよりなるセラミックファイバーが天然ゴムとポリブデンとを組合わせた結合剤でシート状に形成されていることを特徴とする自動車排気ガス浄化器用パツキン。

㉑発明の詳細な説明

この発明は、自動車排気ガス浄化器用パツキンに関するもので、とくにパーミキュライトを原料とする膨張性シート材から構成されるパツキンの改良に関するものである。パーミキュライトを主

加工したパツキン)は、高温に対して優れた耐熱性があり、かつ熱によつて膨張(膨張と呼ばれる)する性質があることから、高温を扱う機器の充填用パツキン材として注目され、その用途開発が行われている。たとえば貴金属触媒を担持させたセラミック製のモノリス型触媒体を金属製筒形容器内に収容して構成される自動車排気ガス浄化器にあつては、前記膨張性シートはモノリス型触媒体(以後モノリスと略称する)と筒形容器(外筒と略称する)との間の充填用として、あるいはモノリスを支持する保持材として使用されている。

上記の自動車排気ガス浄化器に使われている前記モノリスは耐熱、耐熱衝撃、多接触表面積の3つの要求をそれぞれ満足させるように、1.2×10⁻⁶/℃程の低熱膨張率を持つセラミック素地からなり、ハニカム壁0.15mm~0.3mm程の押出し成形品が最適とされているが、この浄化器全体の技術的難点は、モノリスと外筒との間に大きな熱膨張収縮率差があつて、モノリスを外筒内に保持するのに特別な工夫を必要とすることである。特に

最近の傾向として、排気ガス浄化器をエンジン排気マニホールド近傍のより高温部で使用する例が増え、この場合前記外筒材質に熱膨張係数が鋳鋼の1.5倍ある耐熱鋼材を採用したり、前記3つの性能向上を図るため、ハニカム壁が薄くて強度の弱いモノリスの採用を考える場合には、従来にも増して柔らかく、かつクッション性に富むパッキンが要求され、更にモノリスの性能を向上する理由で、モノリスと外筒との間を未浄化排気ガスがバイパスしないようなガスシール性も厳しく要求されるようになってきた。

上記要求を一部あるいはほぼ完全に満すことのできるモノリス用保持材パッキンとして、種々の材質・構造を持つものが提案されており、その一つとして耐熱鋼製のスプリングやベローズで弾力的に保持したり、また同材質の金属細線をメリヤス編みにして圧縮成形したものが、弾力性ある保持材として一部実用化されているが、排気ガスの異状などで、しばしば担持体の温度が過熱して600℃以上の高温になると、スプリングがベローズ成形品は金属の弾力性が失われ、保持材の役目をはたさなくなり、さらに排気ガスの圧力やエンジン等の振動により、モノリスががたつき、最終的に破壊してしまう欠点がある。また前記細線成形品は、排気ガスをシールするには粗すぎて、完全な浄化が期待できない点にも欠点がある。

また、金属材料を使用しない手段としては、耐熱性のある無機質繊維材料をモノリスと外筒との間に充填する手段が提案されており、このものは耐熱温度が高く、またモノリスと外筒との隙間を完全にシールし、未処理排ガスが漏れないことなどが利点とされているが、モノリスをエンジンや走行時の振動や熱冷サイクル下で長期間にわたり有効に保持させるには、パッキンの充填密度を充分高くする必要があり、またパッキン充填に特別な外筒、例えば複数分割型の金属製筒型容器を用意し、モノリスを中にくるんだ厚いマット状繊維材料を強く圧縮し、ネジ・バンド等で固定するような複雑な浄化装置となる欠点がある。

上記手段の改良と考えられるものとして、無機質繊維材料にパーミキュライト粒を抄きこんだパッキンを使用し、これをモノリスと容器との間に充填し、エンジンの排気熱によつてパーミキュライトが膨張して無機質繊維材料を強く圧縮し、そ

れによつてモノリスを保持する手段が提案され、一部実用化されている。しかしながら、このパーミキュライト抄きこみパッキンを実際に充填使用する場合でも、各種条件が厳しくなった現時点では、苛酷な実車条件下で確実にモノリスを保持できる場合は、パッキン厚さの50~60%程度にまで強圧して充填しなければならず、その強圧作用でモノリス側壁を破損する事故がしばしば発生している。

また、さきに本発明は、パーミキュライト粒が熱により膨張する性質をそのまま利用し、パーミキュライト粒をシート化し、セラミックペーパーなどと張り合わせたシートを提案したが、このパッキンは優れた保持力耐久性を示す反面、材質が固く、寸法公差の大きいモノリスの外径寸法を測定して充填量を決め、巻装挿入する工程上の複雑さがある。

本発明者は、前述した各種パッキンの長所短所を検討し、本発明者が先に提案したパーミキュライトシート材が大きな保持力耐久性を発揮する特性を活かし、寸法公差の大きい前記モノリスとそれを保持する外筒との間の狭い隙間に容易に挿入できるほど柔らかく、かつ排気ガス浄化時の高温・エンジン停止時の常温間の熱冷サイクルによる隙間寸法熱膨張繰返し変化下にも長期間にわたつて保持力が保てるパッキンを開発する目的でこの発明を提供したものである。

更に、この発明をなすに到つたきつかけは、本発明者が提案したパーミキュライト粒シートとセラミックファイバーなどのシートが別々に作成しうることに着目し、パーミキュライトを抄きこむシートの製造法では、抄造技術上均一に抄きこめないような大粒のパーミキュライトについても検討し、また多くのセラミックファイバーについて実際の使用状況に近い耐久性試験を繰返して行つたところ、試験初期の保持力は同程度でも長期試験後の保持力に変化が認められ、ある範囲にあるもののみが優れた性能を示すことを見出し、またセラミックファイバー層の弾性結合材として天然ゴムとポリブテンとの組合わせにより、実際の挿入装置に充分適合できる柔軟性・耐屈曲性を付与できることを見出し、その知見にもとづいて、この発明を完成したものである。

この発明において使用されるパーミキュライト

(ひる石)は雲母鉱物の一種で、加熱すると多量に含有する層間水を発散させる過程で原石時の厚さの数倍以上に膨脹してブック状またはアコーディオン状となり、吸音断熱性に富む、嵩高な粒状物が得られることが知られており、これに有機または無機系の種々な結合材を混合したものは建材・耐火材などに多量に利用されている。また、パーミキュライト原石を鉄板などの隙間に充填して加熱膨脹させた板状体はクッション性に富み、自動車用排気ガス浄化器モノリスの保持体として使用できることは、本発明者が先に提案したとおりである。これらのパーミキュライトは、現在南ア・パラボラ産あるいは北米モンタナ産が入手でき、用途に応じて種々の粒径・膨脹程度のものが利用されている。これらパーミキュライト粒の性状を表1に示す。

表 1

南ア	パラボラ産	北米	モンタナ産
4号	3~7メツシュ	#1	3~10メツシュ
3号	5~12メツシュ	#2	8~14メツシュ
2号	9~24メツシュ	#3	10~35メツシュ
1号	16~42メツシュ	#4	28~65メツシュ

また、この本発明で使用されるセラミックファイバーはアルミナとシリカの重量比がほぼ1の配合原料を電弧炉によつて熔融し、高速気流を利用して、あるいは高速回転円板を利用して細繊維化したものである。これらセラミックファイバーは目的とされる耐熱温度により、 $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ 配合比を変え、熔融液の温度・繊維化方式の違いにより、繊維長25~250mm繊維径1.5~6 μ のバルク状集合体として生産され、ガラス軟化温度約850℃、使用温度1100~1500℃の高温用断熱材としてペーパーランケット・紡織品などの形態で利用されている。

この発明によるモノリス型触媒保持用パッキンは基本的には、本発明者が先に提案したパーミキュライトシート即ち未膨脹のパーミキュライト粒と膨脹させたパーミキュライト粒と有機弾性結合材とからなる混合物が0.5~1.5mm程の厚さに加圧成形されたシートであつて、とくにパーミキュライトに所定の粒径のものが選択され、そのシート

の片面もしくは両面にセラミックファイバーと特殊な結合剤とからなる柔軟性に富んだシートが張り付けられた構成に特徴があり、この構成により苛酷な使用条件下でも保持力を失わないよう改良したものである。

この発明の要旨とするところは、パーミキュライトシートとセラミックファイバーシートとを張り合わせて成る自動車排気ガス浄化器用パッキンにおいて、前記パーミキュライトシートは、重量比で1:2~1:5に混合される膨脹されたパーミキュライト粒と粒径35メツシュ以上の未膨脹パーミキュライト粒及び有機弾性結合剤とからなる混合物が所要の面密度をもつてシート状に加圧成形されたものであり、前記セラミックファイバーシートは、アルミナとシリカとからなる組成で平均繊維長50mm以上、平均繊維径2~4 μ よりなるセラミックファイバーが天然ゴムとポリブデンとを組合わせた結合剤でシート状に形成されている自動車排気ガス浄化器用パッキンである。

次にこの発明の内容を、その実施試験に基いて詳細に説明する。

この発明のパッキンが装着される自動車排気ガス浄化器の使用状態は、モノリス外径94.5 \pm 1.5mm、モノリス側壁最高温度600~850℃、金属製外筒内径100mm、最高温度300~350℃で、エンジンの振動による加速度を5G程度受ける例が代表的な例である。モノリスと外筒とのあいだの隙間(2.0~3.5mm)に充填するパッキン量については、パッキンを最小間隙寸法2.0mmに圧縮した時の面圧がモノリス側壁の耐圧強度以上になる量では、モノリスを破壊するおそれがあり、逆に少い場合はモノリスの保持力が低下するので、最小隙間寸法に圧縮したパッキンの面圧がモノリス側壁耐圧強度になる場合を許容最大充填量としてパッキンの試験厚さ(面密度)を決定した。

前記の実車条件を満足させるべく、試験機器・試験方法を検討し、外径93mmの石英ガラス製円筒の外周に試験すべきモノリス用パッキン(25mm巾)を巻き、テーパのついた揺針の底を抜いたような形状の挿入治具を介して内径100mm、肉厚6mmの耐熱鋼製円筒内にパッキンを巻いたモノリスを挿入して試験体とし、この試験体に蓋をして、モノリスが排気ガスに押出される力0.7kgとモノリスが10Gに加振される時に受けると推定される

力(4.2kg)に相当するずり応力がかかるように、耐熱鋼製外筒に錘を加えて常時載荷しておき、加熱冷却は石英ガラス内部より外筒の温度が30分で350℃に昇るように、供給電力量を調節し、続く30分で50℃まで下るように、石英ガラス筒内部より吹きつける圧縮空気量を調節し、この加熱冷却を1サイクルとして繰返して行い、4.9kgの載荷により、石英ガラス筒と耐熱鋼製外筒との間に2mmのずれが生じた時にリミットスイッチが働き、耐久した熱冷サイクルの回数を記録させ、熱冷サイクルを50回耐えた試料を合格とした。なお石英ガラス円筒の熱膨張係数は $0.5 \times 10^{-6}/^{\circ}\text{C}$ で、モノリスの $1.0 \times 10^{-6}/^{\circ}\text{C}$ より小さく、また載荷している荷重も大きく、実車より同等以上の厳しい条件とした。

そこで、モノリスの耐圧強度 $25\text{kg}/\text{cm}^2$ と設定して許容し得る最大の充填量を求めるため、モノリス保持力を要求試験条件に合わせるには、どれ程少量のパーミキュライトで足りるか、またクツシヨン性のあるセラミックファイバーをどれ程多量に組合わせることができるか、下記表2に示す配合量のセラミックファイバーシートおよびパーミキュライトシートを作成して圧縮試験を行い、モノリス・外筒隙間の最小寸法である厚さ2.0mmにおける面圧が $25\text{kg}/\text{cm}^2$ 付近の組合せを選定した。

表 2

試料	セラミックファイバーシートの面密度	パーミキュライトシートの面密度	隙間2.0mmの圧縮応力
(イ)	$1.75\text{kg}/\text{m}^2$	$1.0\text{kg}/\text{m}^2$	$20.3\text{kg}/\text{cm}^2$
(ロ)	1.35	1.35	24.2
(ハ)	0.95	1.80	41.0

(セラミックファイバーシートおよびパーミキ

表

繊維長 繊維径		南ア・パラボラ産		北米モンタナ産			比較例
		3号 5~12mesh	1号 16~42mesh	#2 8~14mesh	#3 10~35mesh	#4 28~65mesh	#4 28~65mesh
50mm	6 μ	× (14)		◎	× (39)		
	2.2 μ	◎	× (9)	◎	◎	× (8)	× (32)

繊維長 繊維径		南ア・パラボラ産		北米モンタナ産			比較例
		3号 5~12mesh	1号 16~42mesh	#2 8~14mesh	#3 10~35mesh	#4 28~65mesh	#4 28~65mesh
	1.5 μ	× (27)		× (45)	× (12)		
32mm	6 μ	× (4)		× (15)			
	2.2 μ	× (8)		◎			
	1.5 μ	× (3)		× (9)			

パーミキュライトシート面密度 1.35kg/ m^2

セラミックファイバー // 1.35 //

括弧内の数字は加熱冷却サイクルの回数。

×印は、石英ガラス製円筒と外筒とのあいだに2mmのずれが生じたもの。

◎印は50回の加熱冷却サイクルでずれが生じなかったもの。

総じてパーミキュライトは粒径の大きなものが有効で、またセラミックファイバーの繊維長は長くて繊維径の2.2 μ 付近のものが優れていることが判明した。また、従来の技術であるパーミキュライト細粒をセラミックファイバーに抄きこんだ場合（配合、シート面密度同等で）をこの発明の例と対比すると、表3の比較例に示すように、保持力耐久性が不足し、苛酷なモノリス用パッキンの条件下では使用できないことが認められた。

* この発明は前記の如くパーミキュライト層とセラミックファイバー層とからなり、未膨張のパーミキュライトが膨張して弾性のある、元厚の数倍の膨張性シートとなることが期待されているため、高熱面であるモノリス側壁に密着して装着されている場合と、パーミキュライト層がモノリス側壁と外筒内壁との中間にある場合とで保持力の耐久性が異なると予想され、モノリス側壁側より「セラミックファイバーシートXkg/ m^2 +パーミキュライトシートYkg/ m^2 +セラミックファイバーシートZkg/ m^2 」の両密度をもつ張り合わせパッキンを下記表4のように作成して耐久試験を行った結果、表中(A)、(B)の組み合わせ時のみ、即ちパーミキュライト層がモノリス側に近い時のみ保持力耐久性があることが判明した。

表

4

	繊維長 // 径 パーミキュライト粒			50mm 2.2 μ 北米モンタナ産 #2	50mm 2.2 μ 北米モンタナ産 #3
	モノリス側 X	外筒側 Y	Z		
A	0	1.35kg/ m^2	1.575kg/ m^2	◎	◎
B	0.20kg/ m^2	1.35kg/ m^2	1.35kg/ m^2	◎	◎
C	0.45kg/ m^2	1.35kg/ m^2	1.13kg/ m^2	× (8)	× (19)
D	0.68kg/ m^2	1.35kg/ m^2	0.90kg/ m^2	× (27)	× (21)

括弧内の数字は加熱冷却サイクルの回数。

×印は、石英ガラス製円筒と外筒とのあいだに

2mmのずれが生じたもの。

◎印は50回の加熱冷却サイクルでずれが生じな

かつたもの。

次にセラミックファイバーの結合剤について述べる。この発明のバツキンにおいては、前述したように、面密度 $1.35\text{kg}/\text{m}^2$ 程のパーミキュライトをシート化する必要がある、これに張り合わされるセラミックファイバーシートは、普通のセラミックファイバーブランケットでは嵩比重が $0.13\text{g}/\text{cm}^3$ であるから、厚さとして 10mm 程で、かつ強度が弱く、モノリス用バツキンとして取扱いができない。またペーパーとして手に入れるものは嵩比重が $0.3\text{g}/\text{cm}^3$ であるから、厚さ 4.5mm で、強度もあるが、前記パーミキュライトシートと張り合わせると、両者合わせて 6mm 程になり、これをモノリス周囲に巻きつけると、外層であるセラミックファイバーペーパーに伸張力がかかり、パーミキュライト層の接着が剥れるか、剥れない場*

*合でもパーミキュライト層にしわが寄る難点が生じた。これらの点を解決するため、種々の結合剤例えばNBR、SBR、NR等のゴム系接着を検討したところ、結局、NRとポリブテン (PB) を組合わせた時のみ上記難点が生じないことを見出した。即ちNRとPBを下記表 5 のように組合わせたものは、同じ面密度のセラミックファイバーのシートでも、シート厚を薄くでき、モノリス径 93mm に屈曲した状態でもパーミキュライトシートとの接着も完全でシートとして伸び易く、またキレツも生じない。特に下記表 5 の例 g のように、NRとPBを倍量に増加したものは、層が薄く面密度が高く、かつ強度も充分あつて、シート柔軟性があり、また良く伸びる性状を示しており、このようなセラミックファイバーシートは、従来存在しなかつたものである。

表

5

	結合剤				厚さ	モノリス周径に曲げた時の所見
	NBR	SBR	NR	PB		
a	7.5%				5.3mm	キレツ発生
b		7.5%			6.9 "	"
c			7.5%		4.5 "	パーミキュライト層・セラミックファイバー層間で剥離
d			5	2.5	4.3 "	"
e			2.5	5	4.0 "	良好
f				7.5	12.0 "	総合力なし
g			5	10	3.5 "	良好

以上の実施試験データをもとに総合した結果を下記実施例として示す。

実施例

平均繊維長 50mm 、平均繊維径 2.2μ のバルク状セラミックファイバー 0.6kg を 100ℓ の試験用ビーターに入れてビーターエッジに荷重をかけずに5分間叩解し、ビーターの底に沈澱した未繊維分(ショット)を除いて、 0.45kg のセラミックファイバーバルブを得て、これに 45g の日本石油精製ポリブテン (HV-300、動粘度 100°F 下32000) とレバーテックス社製天然ゴム (LCSレバーテックス) 22.5g (どちらもエマルジョン) を入れ、アルミナゾル・硫酸バンドを少量入れて定着させ、このセ

ラミックファイバーバルブを $1\text{m} \times 0.33\text{m}$ の手抄き抄造機でシート化し、面圧 $10\text{kg}/\text{cm}^2$ で圧搾して乾燥し、このセラミックファイバーシートの上

に、
3号膨積パーミキュライト粒 (ニチアス製品番号 T / #5888) $\cdots 0.1\text{kg}$
北米モンタナ産パーミキュライト粒 #2 $\cdots 0.35\text{kg}$

NR (LCSレバーテックス60%固形分) $\cdots 0.012\text{kg}$

水 $\cdots 0.070\ell$
を混合した半湿潤粉末を約 5mm 厚に散布し、ローラーで均一に伸展し、その上に $0.2\text{kg}/\text{m}^2$ の面密

13

14

度を持つ前記セラミックファイバーシートと同配合の薄シートをかぶせて組合わせたシート両面を金網ではさみ、面圧 $15\text{kg}/\text{cm}^2$ で加圧し、パーミキュライト半湿潤粉末層からにじみ出したゴムラテックスでシート間を接合し、この積層シートを乾燥させ、 25mm 巾に載断してテープ状とし、モノリス用パッキンとした。

前記パッキンをモノリスに見立てた外径 93mm の石英ガラス製円筒の外周に巻き、テーパのついた播針の底を抜いたような形状の挿入治具を介して内径 100mm 、肉厚 6mm の耐熱鋼製円筒内にパッキンを巻いたモノリスを挿入して試験体とし、この試験体に蓋をして、実際のモノリスが排気ガスに押出される力 0.7kg とモノリスが 10G に加振される時に受けると推定される力(4.2kg)に相当するずり応力がかかるように、耐熱鋼製外筒に錘 4.9kg を加えて常時載荷しておき、加熱冷却は石英ガラス内部より外筒の温度が 30 分で 350°C になるように、供給電力量を調節し、続く 30 分で 50°C まで下るように、石英ガラス筒内部より吹きつける圧縮空気量を調節し、この加熱冷却を 1 サイクルとし、 50 サイクル繰返して行つた後も、石英ガラス筒と外筒との間でずれがなく、合格であった。また前記パッキンをモノリスに前後 2 テープで充填した浄化器を自動車エンジンに組みこみ、

エンジンフル回転 200 時間の台上試験を行つても、モノリスに損傷が認められず、またモノリスがずれた跡も認められず良好であつた。

以上に述べたように、この発明によれば、パーミキュライトシートとセラミックファイバーシートとを張り合わせて成る自動車排気ガス浄化器用パッキンにおいて、前記パーミキュライトシートは、重量比で $1:2 \sim 1:5$ に混合される膨積させたパーミキュライト粒と粒径 35メツシュ 以上の未膨積パーミキュライト粒及び有機弾性結合剤とからなる混合物が所要の面密度をもつシート状に加圧成形されたものであり、前記セラミックファイバーシートは、アルミナとシリカとからなる組成で平均繊維長 50mm 以上、平均繊維径 $2 \sim 4\mu$ よりなるセラミックファイバーが天然ゴムとポリブデンとを組合わせた結合剤でシート状に形成されているものであるから、自動車排気ガス浄化器のモノリスと外筒との隙間に挿入配置するパッキンとして、狭い隙間に容易に挿入させることができ排気ガス浄化時の高温・エンジン停止時の常温間の熱冷サイクルによる隙間寸法熱膨張繰返し変化にも長期間にわたつて適正なモノリス保持力が維持されるパッキンが得られるものであつて、それにより自動車排気ガス浄化器の耐久性向上に大きく寄与することができる。